

App. No. 10/027,677

Amendment mailed December 30, 2003

Re: Office Action mailed July 30, 2003

**REMARKS**

In response to the Office Action mailed July 30, 2003, the Applicant respectfully requests that the Examiner enter the above amendments and consider the following remarks. Claims 6-20 and 24-47 have been withdrawn due to the restriction requirement, and claims 1-4, 21, and 23 have been amended to more clearly describe the invention. New claims 48-54 have been added. As a result, claims 1-5, 21-23, and 48-54 remain pending in the application. The Applicant respectfully requests further examination and reconsideration of the application in light of the amendments and accompanying remarks.

**Rejection of Claim 3 Under 35 U.S.C. § 112**

The Examiner rejected claim 3 under 35 U.S.C. § 112 as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. The Examiner states that this claim recites all possible variables involved in a delayed coking process, without reciting in what fashion or within what metes and bounds each variable is "controlled." The Applicant respectfully traverses this rejection.

**Claim 3 has been modified to distinctly claim the process variables that directly or indirectly impact the ratio of asphaltic coke to thermal coke in the coking portion of the thermal cracking process. The Applicant acknowledges that one having ordinary skill in the art would recognize the group of claim 3 as major**

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variables in the delayed coking process. However, the Applicant respectfully submits that claim 3 is a dependent claim of claim 1, which provides further restrictions regarding the achievement of low ratios of asphaltic coke to thermal coke. Furthermore, the group of claim 3 does not consist of all possible variables involved in a delayed coking process, but only those operational variables that directly or indirectly impact the ratio of asphaltic coke to thermal coke in the coking reactions of the thermal cracking process. The Applicant does not claim to be the first to produce "sponge" coke crystalline structure by altering operational variables of the delayed coking process. Instead, the Applicant has described in the specification of the current invention the various, interrelated factors that impact and determine and impact the ratio of asphaltic coke to thermal coke in the coking reactions of the thermal cracking process, including coker feedstock characteristics and coker operating conditions. Also, the Applicant described how the relationship of these variables change with a particular feedstock, including the integrated use of aromatic feedstocks and quench liquids. Finally, the specification of the current invention thoroughly describes the shortcomings of methods of the prior art to promote the production of sponge coke with feedstocks containing high asphaltenes/resins contents, and the modifications of feed properties and operation variables (group of Claim 3) required to promote the production of sponge coke with such feedstocks. The primary application of these principles allows thermal cracking process users to produce a porous sponge coke

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(while maintaining acceptable coker product yields or improving them) from feedstocks that would predominantly produce shot coke in normal coker operations of the prior art. Shot coke from these feedstocks would not normally allow the desired integration of desirable compounds (e.g., sulfur adsorbents) within the coke crystalline structure. In this novel process, the Applicant has incorporated independent process options that enable the types and degrees of coke fuel improvements to be tailored for a particular coke buyer (e.g., fuel properties, combustion characteristics, and environmental controls). These process options may include new uses or new combinations of inventions of the prior art to achieve very different objectives that are not obvious to one skilled in the art. For example, the specification of the current invention describes new and unexpected results from the integration of highly aromatic slurry oil in the feed while simultaneously quenching the coke drum vapors to substantially decrease the ratio of asphaltic coke to thermal coke and significantly increase the production of sponge coke from feedstocks that would otherwise tend to produce shot coke. Claims 49 to 54 have been added to further specify the control bounds of the group of claim 3. Therefore, the Applicant respectfully submits that the rejection of claim 3 under 35 U.S.C. § 112 cannot be supported.

**Rejection of Claims 1-5 and 21-23 Under 35 U.S.C. § 103(a)**

The Examiner rejected claims 1-5 and 21-23 under 35 U.S.C. § 103(a) as being unpatentable over Meyers (USP 3,917,564) in view of the conventional knowledge in

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the art and further in view of Yan (USP 4,096,097) and Block et al. (USP 5,007,987), with conventional knowledge in the art displayed by the following references for the definition and description of types of cokes:

1. LeCours et al. (USP 6,024,863) Col. 5, Lines 22 - 30 & 63 – 68
2. Greenwalt (USP 5,259,864) Col. 1, Lines 35 - 45
3. Oshol et al. (USP 5,954,949) Col. 1, Lines 65 – Col. 2, Line 20
4. Heck et al. (USP 5,258,115) Col. 1, Lines 60 - 62; Col. 2, Lines 4 - 14
5. Kapner et al. (USP 4,406,872) Col. 1, Lines 28 - 38
6. Hsu et al. (USP 4,291,008) Col. 3, Lines 44 - 49
7. Adams et al. (USP 5,110,448) Col. 1, Lines 29 - 40; Col. 6, Lines 50 - 57

Claims 1-3 were also rejected under 35 U.S.C. § 103(a) as being unpatentable over Schroeder (USP 3,960,701) or Sze et al. (USP 4,326,853) or Grindstaff et al. (USP 4,369,171) or Schlinder et al. (USP 3,852,047) or Hayashi et al. (USP 4,202,868), each in view of Yan (USP 4,096,097) and Block et al. (USP 5,007,987).

Claims 4-5 and 21-23 were also rejected under 35 U.S.C. § 103(a) as being unpatentable over Schroeder (USP 3,960,701) or Sze et al. (USP 4,326,853) or Grindstaff et al. (USP 4,369,171) or Schlinder et al. (USP 3,852,047) or Hayashi et al. (USP 4,202,868), each in view of Yan (USP 4,096,097) and Block et al. (USP 5,007,987) and further in view of Meyers (USP 3,917,564), Scalliet (USP 6,056,882), Bartilucci et al. (USP 4,874,505), Mallari (USP 4,797,197, and Janssen et al. (USP

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4,455,219).

The Applicant respectfully traverses these rejections.

**The current invention is not obvious over Meyers (USP 3,917,564) in view of the conventional knowledge in the art and further in view of Yan (USP 4,096,097) and Block et al. (USP 5,007,987).** Meyers teaches a method of the delayed coking process to dispose of industrial and sanitary wastes, including biological sludges and oily emulsions. These wastes are added to the coke in relatively small quantities to apparently maintain solids levels < 5 wt.% during the quench period of injection. Any incidental increase in VCM level (examples 3-5) is caused by the oil content of the wastes injected. Meyers does not teach a change in crystalline structure effected by reducing or maintaining the ratio of asphaltic coke to thermal coke at a sufficiently low level to produce sponge coke, and does not apparently describe the resulting coke's crystalline structure due to its ultimate objective of wastes disposal. Furthermore, Meyers teaches away from excessive VCM, and does not teach methods to produce sponge coke and the addition of other chemical compounds (e.g., sulfur adsorbents) for the specific purpose of improving the pet coke's combustion characteristics, ash characteristics, and environmental impacts. In addition, Bartilucci et al. (USP 4,874,505) describes the addition of oily sludge in the coke quench and subsequent VCM increase (i.e., Meyers) as undesirable. In contrast, the Applicant teaches methods in the coking process to produce sponge coke with sufficient porosity to

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uniformly distribute various selected additives in the petroleum coke via the coke quench media to improve pet coke fuel properties, combustion characteristics, ash characteristics, and environmental impacts. These methods provide the means to control the quality and quantity of the additives integrated in the modified pet coke. In many cases, injection of these additives requires the increased porosity and improved adsorption characteristics of the pet coke (e.g., coker feedstocks traditionally producing shot coke) created by the methods and process described in the Applicant's specification. First, the Applicant respectfully submits that Meyers does not teach a process or method to produce porous, sponge coke with or without a volatile content of 13-50% by weight. Furthermore, the Applicant respectfully submits that the present invention's controlled injection of selected additives to improve the pet coke's fuel value is distinguished over the injection of sludges and oily emulsions for waste disposal: not only in method, but also as a different purpose or new use.

The Applicant respectfully submits that neither Meyers nor the other references (noted above) teaches a process or method for the production of porous, sponge coke with the VCM content noted. Meyers assumes a "porous coke" (Col. 4; lines 4-5) in his specification and does not describe VCM levels before adding wastes with oil content. LeCours et al. notes a preference for sponge coke, but primarily teaches the addition of certain metals to the coker feedstock to passivate the oxidizing tendencies of the metal impurities inherent in petroleum coke, used in the production of carbon anodes.

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Greenwalt describes the three basic types of pet coke crystalline structure (Shot, Sponge, & Needle), noting that "a typical petroleum coke contains about 10% volatile matter." However, Greenwalt primarily teaches a combustion process with a unique equipment configuration that uses pet coke in the production of molten iron, in a manner that mitigates problems of high sulfur and metals. Oshol et al. also describes the 3 types of coke crystalline structure (at greater length), attributing differences only to the type of feedstock. Oshol et al. teaches an atypical coking process that contacts a molten anhydrous alkali metal hydroxide with heavy petroleum residua to extract substantially all sulfur and heavy metals, while recovering the coke product. Heck et al. also describes the 3 types of coke crystalline structure and attributes differences only to the type of feedstock. Heck et al. teaches the recycling of refinery derived spent caustic by injecting with coker feedstock to induce the production of shot coke. Kapner et al. also discusses sponge coke and needle coke, but teaches a post-coker process to calcine and desulfurize pet coke for the aluminum electrode market (vs. fuel coke). Similarly, Hsu et al. briefly notes a sponge coke with "volatile matter content of 11 wt. %.", but teaches another process to calcine and desulfurize coke for the aluminum electrode market. Adams et al. briefly discusses sponge and needle coke and a stated example of "an effective temperature for initiating the cracking reaction" without sufficient information or context to determine cause and effect (i.e., different temperatures cause different coke crystalline structure) or differences in coker

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feedstocks (i.e., different coke feedstocks require different temperatures to initiate the cracking reaction). However, Adams et al. primarily teaches the use of a water soluble, organic cationic surface active compound to separate oil and water in the coker dewatering system. In summary, none of these references teaches a process or method to produce porous, sponge coke by reducing or mainatining the ratio of asphaltic coke to thermal coke via feedstock additives or changes in process variables.

The Applicant respectfully submits that Yan and Block et al. do not teach processes or methods that produce pet coke with the same type of crystalline structure (via the ratio of asphaltic coke to thermal coke) and specified VCM content or objectives taught by the current invention. Yan teaches a method for the preferential formation of sponge coke (vs. shot coke) which is "suitable for use in the manufacture of electrodes" (emphasis added) via improved grindability characteristics. This is achieved by adding oxygen-containing carbonaceous material to the coker feedstocks. Block et al. states a preference (via a hydrofining process) for a "coking feedstock containing less than about 5 weight percent asphaltenes" to produce needle coke, which typically requires low asphaltenes. Block et al. primarily teaches the reduction of friability in green needle coke by heating the green needle coke external to the coking system and before calcining. In contrast, the current invention teaches the promotion of porous, sponge coke by changing operating conditions and injecting certain additives in the coker heater feed to assure a sufficiently low ratio of asphaltic coke to thermal coke in the

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coking reactions, even with existing levels (e.g., high) of asphaltenes and resins in the coker feedstocks.

The Applicant acknowledges that one having ordinary skill in the art knows that there are three basic types of pet coke crystalline structures produced by the the delayed coking process: shot coke, sponge coke, and needle coke. The Applicant respectfully submits that "regular" or sponge coke is no longer the 'normal product' of the delayed coking process. Over the past years, the coker feedstocks from heavier crudes have yielded as much, if not more, shot coke than "sponge" coke. Due to its "shot" crystalline structure (hard spheres), sulfur content, and troublesome metals, this type of pet coke typically goes to a low-value fuel market, as one of the poorest fuels available. This shot coke does not allow the desired integration of desirable compounds within the coke crystalline structure. The Applicant does not claim to be the first to produce "sponge" coke crystalline structure. Instead, the Applicant has described in the specification of the current invention the various, interrelated factors that determine the three basic types of coke crystalline structures, including coker feedstock characteristics and coker operating conditions. Also, the Applicant described the transitions, hybrids, and mixtures of these coke crystalline structures, including general porosity properties and adsorption characteristics. Finally, the specification of the current invention thoroughly describes the shortcomings of the fuel-grade coke of the prior art, and the modifications in fuel properties, combustion characteristics, ash

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characteristics, and environmental controls necessary to increase its value to traditional coal-fired facilities in the fuel market. The primary application of these principles allows thermal cracking process users to produce a porous sponge coke (while maintaining acceptable coker product yields or improving them) from feedstocks that would predominantly produce shot coke in normal coker operations of the prior art. Shot coke from these feedstocks would not normally allow the desired integration of desirable compounds (e.g., sulfur adsorbents) within the coke crystalline structure. In this novel process, the Applicant has incorporated independent process options, that allow the types and degrees of coke fuel improvements to be determined for a particular coke buyer (e.g., fuel properties, combustion characteristics, ash characteristics, and environmental controls). These process options may include new uses or new combinations of inventions of the prior art to achieve very different objectives that are not obvious to one skilled in the art. For example, the specification of the current invention describes new and unexpected results from the integration of sulfur sorbents within the very porous structure of the modified pet coke (i.e., vs. sorbent injection into the firebox of the prior art in the field of coal combustion).

In the description, the VCM level of the coke itself is used as a basic operational indicator of when sufficient aromatics (vs. resins & asphaltenes) exist within the coke crystalline structure to create the desired porosity characteristics for the uniform distribution of desirable additives to improve the pet coke's fuel properties, combustion

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characteristics, ash characteristics, and environmental controls. This target VCM level will be different for different feedstock characteristics. That is, increasing the porosity and adsorption character from normal sponge coke increases the percent solids that can be added to the quench water and pet coke. However, the specification also warns of other VCMs in the pet coke pores that were not true indicators of the pet coke crystalline structure. For example, pet coke VCM levels can be readily increased to levels > 13 wt%, simply by reducing steaming in the quench cycle that normally removes heavy oils trapped in the pores of the sponge coke. Similarly, other VCMs are not intended indicators of the modified pet coke's crystalline structure: the use of quench media by the current invention to intentionally add specific quantities of high-quality and low-quality VCMs to initiate and sustain pet coke combustion. Consequently, pet coke with VCM content >13 wt% may be found in various patents and other references. However, the prior art of delayed coking teaches away from VCM levels exceeding 12 wt.% due to detrimental impacts on coke calcining and coker product yields. Only after the knowledge presented in the specification of the current invention (e.g., novel principles of how these additives improve the pet coke's fuel properties, combustion characteristics, ash characteristics, and environmental impacts) can the uniform integration of desirable additives in a porous coke crystalline structure with specified VCMs in the coke produce the new and unexpected results of the current invention.

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The Applicant respectfully submits that any such combination would not be obvious to one skilled in the art. The combination of Meyers' disposal of wastes in the pet coke (via quench water), Yan's promotion of sponge coke suitable for the manufacture of electrodes, Block et al.'s reduction of green needle coke friability, and conventional knowledge in the art (i.e., sponge coke crystalline structure) is submitted to be improper because this combination would not teach the claims of this invention. Furthermore, Meyers, Yan, Block et al, and conventional knowledge in the art do not suggest such a combination, and one skilled in the art would have no reason to make such a combination. Meyers, Yan, or Block et al. do not teach or suggest a thermal cracking process or method to produce a sponge coke via sufficiently low ratio of asphaltic coke to thermal coke with VCM levels > 13 wt.% within the coke crystalline structure to indicate higher porosity and improved adsorption characteristics. Likewise, conventional knowledge in the art does not teach or suggest a controlled, uniform integration of desirable additives via the thermal cracking process quench. Furthermore, neither Meyers nor conventional knowledge in the art teach or suggest the potential use of increased porosity and improved adsorption characteristics of the coke produced to add chemical compounds to the coke in the quenching portion of the thermal cracking process. Accordingly, there is no motivation in the prior art to combine the references as suggested by the Examiner, and the proposed combination of these references still does not teach or suggest every limitation of the present invention.

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In conclusion, the Applicant respectfully submits that the novel thermal cracking process options and methods of the current invention are (1) unobvious to one skilled in the art and (2) these distinctions of the present invention provide surprising and unexpected results and are patentable under Section 103 because the production of porous, sponge coke via controlling the ratio of asphaltic coke to thermal coke for a given coker feedstock provides increased porosity and improved adsorption characteristics of the modified coke to allow the integration of various desirable chemical compounds (e.g., sulfur adsorbents, high quality VCM, and oxygen-containing hydrocarbons) during the quench of the thermal cracking process (e.g., delayed coking) which can improve the coke's fuel properties, combustion characteristics, and environmental impacts. Therefore, Meyers, Yan, Block et al. and conventional knowledge in the art provide no motivation to combine or modify the references as suggested by the Examiner in order to arrive at the claimed invention.

**Claims 1-3 of the Current Invention are Not Obvious from the Combination of Various Cited References in the Prior Art.** Claims 1-3 were rejected as being unpatentable over Schroeder (USP 3,960,701) or Sze et al. (USP 4,369,171) or Grindstaff et al. (USP 4,369,171) or Schlinger et al. (USP 3,852,047) or Hayashi et al. (USP 4,369,171) each in view of Yan (USP 4,096,097) and Block et al. (USP 5,007,987). The Applicant respectfully submits that any combination of these references would not be obvious to one skilled in the art. Furthermore, Schroeder, Sze

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et al, Grindstaff et al, Schlinder et al, and Hayashi et al. do not teach processes or methods that produce pet coke with the same type of crystalline structure, ratio of asphaltic coke to thermal coke, and VCM content taught by the current invention. Similarly, Block et al. and Yan do not achieve the objectives or the claim limitations of the current invention. Any combination of these various references is submitted to be improper because none of these references suggest any such combination, and one skilled in the art would have no reason to make such a combination. Only after the knowledge presented in the specification of the current invention (e.g., novel principles of how these additives improve the pet coke's fuel properties, combustion characteristics, ash characteristics, and environmental controls) can the thermal coking process modifications and feedstock additives be used to produce the porous, sponge coke crystalline strucure with specified VCMs in the coke to produce new and unexpected results of the current invention by uniform integration of desirable additives.

The Applicant respectfully submits that Schroeder, Sze et al., Grindstaff et al., Schlinder et al., and Hayashi et al. do not teach processes or methods that produce pet coke with the same type of crystalline structure and specified VCM content or objectives taught by the current invention. Schroeder teaches the conversion of non-coking coals to coking coals by hydrogenation at much higher pressures than the current invention (500 to 4000 psi vs. <100 psi), and does not describe the resulting pet coke's crystalline structure nor the nature of the VCM contained therein. Apparently, Schroeder does not

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address these issues due to its ultimate objective of producing a high-density (i.e., non-porous) coke with very low VCM (e.g., < 3%) after calcining for the manufacture of electrodes for the steel industry. Similarly, Sze et al. uses a high-pressure coal liquefaction process to develop a "soft" coke with 16-30 wt.% VCM content. Sze et al. describes heater outlet temperature controls as the only means to effect such coke. Using only heater outlet temperature control to achieve these high VCM levels can lead to unmanageable pitch content of the resulting coke, as described by the Applicant in the specification of the current invention. Again, Sze et al. does not apparently describe the resulting coke's crystalline structure nor the nature of the coke's VCM due to its ultimate objective of blending this coke with bituminous coal to be carbonized (i.e., non-porous structure w/< 3 wt.% VCM) for use as metallurgical coke. Grindstaff et al. does not teach the production of very porous sponge coke with VCM > 13 wt.%, but teaches the reduction of pet coke VCM levels via hot solvent extraction. Apparently, the hot extraction is not effective unless the pet cokes VCM levels exceed 10 wt.%. Since VCMs tied up in the coke crystalline structure would not be readily extracted, one skilled in the art can conclude that the high levels of VCM in Table 1 are a result of poor coker process steaming practices, which are used to extract trapped oils (VCMs) on the surface of the coke within the coking process. As such, Grindstaff et al. does not teach a change in crystalline structure effected by maintaining a low ratio of asphaltic coke to thermal coke and/or an increase in VCM in the pet coke, and does not apparently

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describe the resulting coke's crystalline structure nor the nature of the coke's VCM due to its ultimate objective of producing carbon anodes (i.e., non-porous structure w/ < 3 wt.% VCM) for Hall aluminum cells. Schlänger teaches "manufacturing clusters of petroleum coke pellets which are characterized by unusually high density and low porosity" (col. 1, lines 33-40). Though the seeding particles are "sponge-like," the crystalline structure of the high-density clusters of the product coke pellets is more like the consistency of shot coke or fluid coke than sponge coke. As noted in col. 10, lines 48-58, the high levels of VCM in Table 2 are the result of poor coker process steaming practices, which are used to extract trapped oils (VCMs) on the surface of the coke within the coking process. As such, Schlänger does not teach a change in crystalline structure effected by maintaining a low ratio of asphaltic coke to thermal coke and/or an increase in VCM in the pet coke, and does not apparently describe the resulting coke's crystalline structure nor the nature of the coke's VCM due to its ultimate objective of use in metallurgical processes, including blast furnace coke. Finally, Hayashi et al. teaches "the production of high-density carbon materials" (Abstract). As noted in col. 5, lines 1-5, the high levels of VCM in claim 6 are the result of poor coker process steaming practices, which are used to extract trapped oils (VCMs) on the surface of the coke within the coking process. As such, Hayashi et al. does not teach a change in crystalline structure effected by maintaining a low ratio of asphaltic coke to thermal coke and/or an increase in VCM in the pet coke, and does not apparently describe the

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resulting coke's crystalline structure due to its ultimate objective of use in a process for making high-density carbon materials, for various uses other than fuel. In summary, none of these cited references teaches a change in crystalline structure effected by maintaining a low ratio of asphaltic coke to thermal coke and/or an increase in the VCM of the pet coke.

The Applicant respectfully submits that Yan and Block et al do not achieve the objectives or the claim limitations of the current invention. As noted previously, Yan teaches a method for the preferential formation of sponge coke (vs. shot coke) "suitable for use in the manufacture of electrodes" via improved grindability characteristics. This is achieved by adding oxygen-containing carbonaceous material to the coker feedstocks. Block et al. states a preference (via a hydrofining process) for a "coking feedstock containing less than about 5 weight percent asphaltenes" to produce needle coke, which typically requires very low asphaltenes. Block et al. primarily teaches the reduction of friability in green needle coke by heating the green needle coke external to the coking system and before calcining. In contrast, the current invention teaches the promotion of porous, sponge coke by changing operating conditions and injecting certain additives in the coker heater feed to assure a sufficiently low ratio of asphaltic coke to thermal coke in the coking reactions, even with existing levels (e.g., high) of asphaltenes and resins in the coker feedstocks. The Applicant also incorporates some principles of this expired patent (Yan) in the specification of the current invention in a

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novel combination of methods and "new use" for increasing the porosity and adsorption character of the pet coke to improve the ability to uniformly distribute desirable additives into the modified pet coke. In turn, uniform integration of these additives has the objective of improving the fuel properties, combustion characteristics, ash characteristics, and/or environmental impacts of the modified pet coke, not manufacture of electrodes.

The Applicant respectfully submits that none of these cited references teaches controlling the ratio of asphaltic coke to thermal coke as a method to produce porous, sponge coke, even with coker feedstocks (e.g., high asphaltenes and resins contents) that predominantly form shot coke in coker operations of the prior art. The Applicant respectfully submits that any combination of these cited references would not be obvious to one skilled in the art. The combination of porous "sponge" coke with VCM content > 13 wt.% and the modification of coker feedstock characteristics (via hydrofining and adding oxygen-containing carbonaceous material) for improving the pet coke's combustion characteristics and environmental impacts is submitted to be improper because none of the cited references suggest such a combination, and one skilled in the art would have no reason to make such a combination. Furthermore, none of the cited references teach or suggest the potential use of increased porosity and improved adsorption characteristics of a modified coke to add chemical compounds to the coke in the quenching portion of the thermal cracking process. Accordingly, there

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is no motivation in the prior art to combine the references as suggested by the Examiner, and the proposed combination of these references still does not teach or suggest every limitation of the present invention. These distinctions of the present invention provide surprising and unexpected results and are patentable under Section 103 because the improved adsorption characteristics of the modified coke allow the integration of various desirable chemical compounds (e.g., sulfur adsorbents, high quality VCM, and oxygen-containing hydrocarbons) during the quench of the thermal cracking process (e.g., delayed coking) which can improve the coke's fuel properties, combustion characteristics, and environmental impacts. Therefore, none of the cited references provide any motivation to combine or modify the references as suggested by the Examiner in order to arrive at the claimed invention.

Since the novel physical features of the applicant's modified petroleum coke provide these new and unexpected results over any reference, the Applicant submits that these new results indicate unobviousness and hence patentability. Therefore, the Applicant respectfully submits that no combination of the cited references can support the rejection of claims 1-3 under 35 U.S.C. § 103(a). Accordingly, the Applicant respectfully requests reconsideration and allowance of the present application with the above-amended claims.

**Claims 4-5 and 21-23 of the Current Invention are Not Obvious from the Combination of Various Cited References in the Prior Art.** Claims 4-5 and 21-23

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were rejected as being unpatentable over Schroeder (USP 3,960,701) or Sze et al. (USP 4,369,171) or Grindstaff et al. (USP 4,369,171) or Schlinger et al. (USP 3,852,047) or Hayashi et al. (USP 4,369,171) each in view of Yan (USP 4,096,097) and Block et al. (USP 5,007,987) and further in view of Meyers (USP 3,917,564), Scalliet (USP 6,056,882), Bartilucci et al. (USP 4,874,505), Mallari (USP 4,797,197), and Janssen et al. (USP 4,455,219). The Applicant respectfully submits that any combination of these references would not be obvious to one skilled in the art. Furthermore, Schroeder, Sze et al., Grindstaff et al., Schlinger et al., and Hayashi et al. do not teach processes or methods that produce pet coke with the same type of crystalline structure, thermal and reaction quench, ratio of asphaltic coke to thermal coke, and VCM content taught by the current invention. Similarly, Block et al., and Yan do not teach the same type of thermal and reaction quench and achieve neither the objectives nor the claim limitations of the current invention. Any combination of these various references is submitted to be improper because none of these references suggest any such combination, and one skilled in the art would have no reason to make such a combination. Only after the knowledge presented in the specification of the current invention (e.g., novel principles of how to use a novel thermal and/or chemical reaction quench) can the thermal coking process modifications and feedstock additives be used to produce the porous, sponge coke crystalline structure with the low ratio of asphaltic coke to thermal coke and specified VCMs in the coke to produce new and

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unexpected results of the current invention and to provide the uniform integration of desirable additives.

The Applicant respectfully submits that Schroeder, Sze et al., Grindstaff et al., Schlenger et al., and Hayashi et al. do not teach processes or methods that produce pet coke with the same type of crystalline structure and specified VCM content or objectives taught by the current invention. Schroeder teaches the conversion of non-coking coals to coking coals by hydrogenation at much higher pressures than the current invention (500 to 4000 psi vs. <100 psi), and does not describe the resulting pet coke's crystalline structure nor the nature of the VCM contained therein. Apparently, Schroeder does not address these issues due to its ultimate objective of producing a high-density (i.e., non-porous) coke with very low VCM (e.g., < 3%) after calcining for the manufacture of electrodes for the steel industry. Similarly, Sze et al. uses a high-pressure coal liquefaction process to develop a "soft" coke with 16 – 30 wt.% VCM content. Sze et al. describes heater outlet temperature controls as the only means to effect such coke. Using only heater outlet temperature control to achieve these high VCM levels can lead to unmanageable pitch content of the resulting coke, as described by the Applicant in the specification of the current invention. Again, Sze et al. does not apparently describe the resulting coke's crystalline structure nor the nature of the coke's VCM due to its ultimate objective of blending this coke with bituminous coal to be carbonized (i.e., non-porous structure w/< 3 wt.% VCM) for use as metallurgical coke. Grindstaff et al.

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does not teach the production of very porous sponge coke with VCM > 13 wt.%, but teaches the reduction of pet coke VCM levels via hot solvent extraction. Apparently, the hot extraction is not effective unless the pet coke's VCM levels exceed 10 wt.%. Since VCMs tied up in the coke crystalline structure would not be readily extracted, one skilled in the art can conclude that the high levels of VCM in Table 1 are a result of poor coker process steaming practices, which are used to extract trapped oils (VCMs) on the surface of the coke within the coking process. As such, Grindstaff et al. does not teach a change in crystalline structure effected by maintaining a low ratio of asphaltic coke to thermal coke and/or an increase in VCM in the pet coke, and does not apparently describe the resulting coke's crystalline structure nor the nature of the coke's VCM due to its ultimate objective of producing carbon anodes (i.e., non-porous structure w/ < 3 wt.% VCM) for Hall aluminum cells. Schlanger teaches "manufacturing clusters of petroleum coke pellets which are characterized by unusually high density and low porosity" (col. 1, lines 33-40). Though the seeding particles are "sponge-like," the crystalline structure of the high-density clusters of the product coke pellets is more like the consistency of shot coke or fluid coke than sponge coke. As noted in col. 10, lines 48-58, the high levels of VCM in Table 2 are the result of poor coker process steaming practices, which are used to extract trapped oils (VCMs) on the surface of the coke within the coking process. As such, Schlanger does not teach a change in crystalline structure effected by maintaining a low ratio of asphaltic coke to thermal coke and/or an

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increase in VCM in the pet coke, and does not apparently describe the resulting coke's crystalline structure nor the nature of the coke's VCM due to its ultimate objective of use in metallurgical processes, including blast furnace coke. Finally, Hayashi et al. teaches "the production of high-density carbon materials" (Abstract). As noted in col. 5, lines 1-5, the high levels of VCM in Claim 6 are the result of poor coker process steaming practices, which are used to extract trapped oils (VCMs) on the surface of the coke within the coking process. As such, Hayashi et al. does not teach a change in crystalline structure effected by maintaining a low ratio of asphaltic coke to thermal coke and/or an increase in VCM in the pet coke, and does not apparently describe the resulting coke's crystalline structure due to its ultimate objective of use in a process for making high-density carbon materials, for various uses other than fuel. In summary, none of these cited references teaches a change in crystalline structure effected by maintaining a low ratio of asphaltic coke to thermal coke and/or an increase in the VCM of the pet coke.

The Applicant respectfully submits that Yan and Block et al do not achieve the objectives or the claim limitations of the current invention. As noted previously, Yan teaches a method for the preferential formation of sponge coke (vs. shot coke) "suitable for use in the manufacture of electrodes" via improved grindability characteristics. This is achieved by adding oxygen-containing carbonaceous material to the coker feedstocks. Block et al. states a preference (via a hydrofining process) for a "coking

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feedstock containing less than about 5 weight percent asphaltenes" to produce needle coke, which typically requires very low asphaltenes. Block et al. primarily teaches the reduction of friability in green needle coke by heating the green needle coke external to the coking system and before calcining. In contrast, the current invention teaches the promotion of porous, sponge coke by changing operating conditions and injecting certain additives in the coker heater feed to assure a sufficiently low ratio of asphaltic coke to thermal coke in the coking reactions, even with existing levels (e.g., high) of asphaltenes and resins in the coker feedstocks. The Applicant also incorporates some principles of this expired patent (Yan) in the specification of the current invention in a novel combination of methods and "new use" for increasing the porosity and adsorption character of the pet coke to improve the ability to uniformly distribute desirable additives into the modified pet coke. In turn, uniform integration of these additives has the objective of improving the fuel properties, combustion characteristics, ash characteristics, and/or environmental impacts of the modified pet coke, not the manufacture of electrodes.

The Applicant respectfully submits that Meyers, Scalliet, Bartilucci et al, Mallari, and Janssen et al. do not achieve the objectives or the claim limitations of the current invention. Meyers teaches a method of the delayed coking process to dispose of industrial and sanitary wastes, including biological sludges and oily emulsions. Apparently, these wastes are added to the coke in relatively small quantities to maintain

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solids levels < 5 wt.% during the quench period of injection. Any incidental increase in VCM level (examples 3-5) is caused by the oil content of the wastes injected. Meyers does not teach a change in crystalline structure effected by an increase in VCM in the pet coke, and does not apparently describe the resulting coke's crystalline structure due to its ultimate objective of wastes disposal. Furthermore, Meyers teaches away from excessive VCM levels, and does not teach controlling of the ratio of asphaltic coke to thermal coke to produce porous, sponge coke that allows the addition of other chemical compounds (e.g., sulfur adsorbents) for the specific purpose of improving the pet coke's combustion characteristics, ash characteristics, and/or environmental impacts. Scalliet teaches the application of shear forces via various types of mills to separate oil from water and solids in a "tight" emulsion, often existing in waste sludges. The resulting "solids slurry" (water w/solids) can be used as the coker quench media. Scalliet does not teach the controlling of the ratio of asphaltic coke to thermal coke to produce porous, sponge coke that allows the addition of desirable additives to improve (in various degrees) the fuel properties, combustion characteristics, ash characteristics and/or environmental impacts of the pet coke. Bartilucci et al. (USP 4,874,505) describes the addition of oily sludge in the coke quench (i.e., Meyers) as undesirable, and teaches the segregation of waste sludges according to oil content. Only non-oily wastes are injected in the coke quench to avoid the "undesirable" addition of VCMs in Meyers. Bartilucci et al. does not teach the controlling of the ratio of asphaltic coke to

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thermal coke to produce porous, sponge coke that allows the addition of desirable additives to improve (in various degrees) the fuel properties, combustion characteristics, ash characteristics, and/or environmental impacts of the pet coke.

Mallari teaches the use of a "flasher drum" between the feed heater and the coke drums of the delayed coking process of the prior art to extract vapors present at the heater outlet to reduce the coking reactions of heavy hydrocarbons and produce less coke. The injection of hydrogen gas in this flasher drum is used to increase hydropyrolysis in the flasher drum by operating at higher hydrogen partial pressure, higher temperature, and higher residence time. Mallari also teaches increasing heater outlet temperature and lower coke drum pressure (vs. delayed coking of the prior art); the opposite direction of exemplary embodiments of the current invention. Mallari does not teach the use of a third drum for adding an additional process cycle to the thermal cracking process (e.g., delayed coking) of the prior art. Furthermore, Mallari does not teach the injection of hydrogen in the coking vessels to (1) increase coke porosity, (2) chemically quench undesirable cracking (e.g., vapor cracking) or coking reactions, and/or (3) induce hydrogenation or hydrolysis reactions to increase the yield of valuable hydrocarbons and coke porosity. Janssen et al. teaches the minimization of coke yield by minimizing normal heavy recycle in delayed coking of the prior art and adding a lower boiling range stream from the coker fractionator as recycle. Janssen et al. describes the use of a small amount of heavy coker gas oil to quench the vapors from

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the coke drums ("between the coke drum and the fractionator") to prevent coke deposition in the vapor lines. Janssen et al. does not teach the use of aromatic additives in the feed to effect porous sponge coke via controlling the ratio of asphaltic coke to thermal coke. Furthermore, Janssen et al. does not teach the use of heavy coker gas oil to thermally quench the vapors inside or at the exit of the coke drum to reduce vapor cracking reactions and lower the ratio of asphaltic coke to thermal coke in the coking reactions within the coking vessel (e.g., coke drum of the delayed coking process). In contrast, the Applicant teaches the use of various quench media (e.g., hydrogen, heavy coker gas oil) to thermally and/or chemically quench the vapors inside or at the exit of the coke drum to reduce vapor cracking reactions and lower the ratio of asphaltic coke to thermal coke in the coking reactions within the coking vessel (e.g., coke drum of the delayed coking process). In addition, the Applicant teaches the reduction of heater outlet temperature, reduction of coking vessel temperature, and increasing coking vessel pressure as methods to lower the ratio of asphaltic coke to thermal coke in the coking reactions within the coking vessel.

The Applicant respectfully submits that none of these cited references teaches the controlling the ratio of asphaltic coke to thermal coke as a method to produce porous, sponge coke, even with coker feedstocks (e.g., high asphaltenes and resins contents) that predominantly form shot coke in coker operations of the prior art. The Applicant respectfully submits that any combination of these cited references would not

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be obvious to one skilled in the art. The combination of (1) porous "sponge" coke with VCM content > 13 wt.% and (2) the modification of coker feedstock characteristics (via hydrofining and adding oxygen-containing carbonaceous material) and (3) the use of quench oil between the coke drum and fractionator to reduce coke deposition in vapor lines for improving the pet coke's combustion characteristics, ash characteristics, and environmental impacts is submitted to be improper because none of the cited references suggest such a combination, and one skilled in the art would have no reason to make such a combination. Furthermore, none of the cited references teach or suggest the potential use of increased porosity and improved adsorption characteristics of a modified coke to add chemical compounds to the coke in the quenching portion of the thermal cracking process. Accordingly, there is no motivation in the prior art to combine the references as suggested by the Examiner, and the proposed combination of these references still does not teach or suggest every limitation of the present invention. These distinctions of the present invention provide surprising and unexpected results and are patentable under Section 103 because the porous sponge coke and the improved adsorption characteristics of the modified coke allow the integration of various desirable chemical compounds (e.g., sulfur adsorbents, high quality VCM, and oxygen-containing hydrocarbons) during the quench of the thermal cracking process (e.g., delayed coking) which can improve the coke's fuel properties, combustion characteristics, ash characteristics, and environmental impacts.

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Therefore, none of the cited references provide any motivation to combine or modify the references as suggested by the Examiner in order to arrive at the claimed invention.

Since the novel physical features of the applicant's modified petroleum coke provide these new and unexpected results over any reference, the Applicant submits that these new results indicate unobviousness and hence patentability. Therefore, the Applicant respectfully submits that no combination of the cited references can support the rejection of claims 4-5 and 21-23 under 35 U.S.C. § 103(a). Accordingly, the Applicant respectfully requests reconsideration and allowance of the present application with the above-amended claims.

**Rejection of Claims 4, 5, and 21-23 Under Double Patenting Doctrine**

Claims 4, 5, and 21-23 were rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-21 of U.S. Patent No. 6,168,709 in view of Meyers (USP 3,917,564), Scalliet (USP 6,056,882), or Bartilucci et al. (USP 4,874,505). The Applicant respectfully traverses the rejection. The Applicant respectfully submits that claim 1 has been amended and distinguished over claims 1-21 of U.S. Patent No. 6,168,709. None of the secondary references teach controlling of the ratio of asphaltic coke to thermal coke to increase porosity and improve adsorption characteristics of coke to add chemical compounds to the pet coke in the quenching portion of the thermal cracking process. Furthermore, none of the cited references provide any motivation to combine or modify the references as

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suggested by the Examiner in order to arrive at the claimed invention. Therefore, the Applicant respectfully submits that claims 1-21 of U.S. Patent No. 6,168,709 in view of Meyers (USP 3917564), Scalliet (USP 6056882), or Bartilucci et al. (USP4874505) cannot support the rejection of claims 4, 5, and 21-23 under the obviousness-type double patenting doctrine.

Claims 4, 5, and 21-23 were provisionally rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 23-33 of copending Application No.09/763,282. The Applicant respectfully traverses the rejection. The Applicant respectfully submits that claims 23-33 of copending Application No. 09/763,282 do not teach controlling the ratio of asphaltic coke to thermal coke or injecting thermal or chemical reaction quenches to reduce cracking of valuable hydrocarbons in the vapor phase (e.g., vapor overcracking). The independent claims of this continuation-in-part contain these limitations, which are not contained in the claims of the copending application. Therefore, the Applicant respectfully submits that claims 23-33 of Application No. 09/763,282 cannot support the rejection of claims 4, 5, and 21-23 under the obviousness-type double patenting doctrine.

Claims 4, 5, and 21-23 were provisionally rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-44 of copending Application No.09/556,132. The Applicant respectfully traverses the rejection. The Applicant respectfully submits that claims 1-44 of copending Application

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No. 09/556,132 do not teach controlling the ratio of asphaltic coke to thermal coke or injecting thermal or chemical reaction quenches to reduce cracking of valuable hydrocarbons in the vapor phase (e.g., vapor overcracking). The independent claims of this continuation-in-part contain these limitations, which are not contained in the claims of the copending application. Therefore, the Applicant respectfully submits that claims 1-44 of Application No. 09/556,132 cannot support the rejection of claims 4, 5, and 21-23 under the obviousness-type double patenting doctrine.

### Conclusion

The Applicant has distinguished claims 1-5, 21-23, and 48-54 over the cited references. Therefore, the Applicant respectfully submits that the present application is now in condition for allowance, and such action is earnestly requested.

Respectfully submitted,

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